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Comparison of MEA degradation in pilot-scale with lab-scale experiments

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Abstract

To understand which part of the CO_2 amine-based system is mostly responsible of amine degradation, MEA degradation under real CO_2 capture conditions is compared with two laboratory experiments; a thermal degradation experiment representative of the stripper conditions (MEA 30 wt %, CO_2 loaded, α = 0.5, 135 °C) and an oxidative degradation experiment representative of the absorber conditions (MEA 30 wt %, CO_2 loaded, α = 0.4, sparged with air + CO_2, 55 °C). Liquid Chromatography – Mass Spectrometry (LC-MS) was used for the quantification of the remaining amine and Gas Chromatography – Mass Spectrometry (GC-MS) was used for the identification and quantification of the main degradation compounds. This study suggests that MEA degradation in the pilot plant is more dominated by oxidative degradation than by thermal degradation. It is also found that reactions between MEA and carboxylic acids present in the solution may play a significant role in solvent degradation. This implies that carboxylic acids, usually referred to as "Heat Stable Salts", are not stable and can react further to give more complex compounds.

Keywords: MEA degradation, absorber and stripper conditions, pilot plant

1. Introduction

Post-combustion CO_2 capture is currently a very attractive technology for the treatment of flue gases produced in existing power plants. Amine-based CO_2 capture systems are based on reversible chemical reactions between CO_2 and an aqueous amine solution. Among the numerous absorbents screened for this application, monoethanolamine (MEA) is so far considered as the benchmark solvent owing to its good properties towards CO_2 (fast absorption rate, cheap, not volatile). However, MEA is not flawless: in addition to a high energy requirement in the stripping stage, its degradation and corrosivity are important issues for industrial application resulting in additional costs.

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For the purposes of improving a MEA based process and developing better solvent systems, it would be useful to understand the chemistry of MEA degradation. This entails identifying the degradation products formed and understanding how they are formed. Understanding of amine degradation is also very important for environmental reasons since the degradation compounds can be released from the pilot plant into the atmosphere. However, the study of amine degradation is not an easy task. It is difficult to set up a lab-scale experiment representative of the dynamic cycling system of the solvent between the absorber and the stripper. In the real process, the solvent is subject to varying conditions (temperature, gas composition) which can lead to different kinds of degradation in the various parts. In fact, two main forms of degradation are expected to occur in a CO_2 capture plant: degradation due to temperature and CO_2 is more likely to proceed in the stripper where the highest temperatures are encountered (around 120 °C for MEA), while oxidative degradation is mostly expected in the absorber since the O_2 concentration is there the highest. MEA degradation has been studied since the 1950's.[1] Both the thermal degradation due to CO_2 [2-3] and the oxidative degradation [4-6] have been the subject of studies, but the understanding of these phenomena is still incomplete. We are only aware of a single study in the open scientific literature regarding MEA degradation in a post combustion CO_2 capture plant.[7]

This present paper reports a study of MEA degradation under real CO_2 capture conditions and the comparison with two relevant lab experiments, chosen to be as close as possible to the absorber and stripper conditions respectively. A list of the main degradation compounds identified is reported in Appendix A.

Degraded samples of MEA from a real pilot plant were provided by the CESAR project. The pilot plant at Esbjergværket (ESV) in Denmark has been used to test the performance of new energy efficient solvents.[8] The pilot plant operates on a slipstream of flue gas from a 400 MW pulverised coal-fired power station. The plant has SCR DeNOx, electrostatic precipitators (ESP) and a Flue Gas Desulfurization (FGD) processes to clean the flue gases before treatment. In 2009, a 3360-hours (20 weeks) test campaign was conducted at ESV using the benchmark solvent, MEA at 30 weight %. Liquid samples of the solvent were taken in different parts of the process and analyzed.

These samples were compared with two lab-experiments to understand which part of the process is responsible for MEA degradation. The effect of CO_2 content was investigated in closed-batch at high temperature (135 °C) and oxidative degradation was performed in open-batch at 55 °C by sparging with a gas blend of CO_2 and O_2.

All samples were analyzed in the same way: amine loss was determined by Liquid Chromatography – Mass Spectrometry (LC-MS) and the main degradation compounds were identified and quantified by Gas Chromatography – Mass Spectrometry (GC-MS).

2. Experimental section

2.1. MEA Campaign at the Esbjerg pilot plant

MEA as absorbent was tested for more than 3300 hours of piloting (equivalent to 20 weeks) at Esbjerg. After 11 weeks of operation, liquid samples were taken in the different parts of the pilot: the lean amine in the absorber, the rich amine in the stripper, and the water washes (both for the absorber and stripper). In addition, the final lean MEA solution corresponding to the end of the campaign was analyzed.

2.2. Lab-scale experiments

2.2.1. Thermal degradation

A 30 wt % aqueous solution of MEA was prepared by using deionised water. After degassing with nitrogen for 15 min in order to strip any air contamination, the solution was loaded with 0.5 mole of CO_2 per mole of amine. 7 mL of the solution was then introduced in 316 stainless steel cylinders, which were put into a Memmert oven (model 600) from GmBH+Co. The cylinders were heated for 5 weeks at 135 °C. At regular intervals (every week), one cylinder was taken and analyzed by the following analytical procedures. Potential leakages were also checked by weight comparison of each cylinder before and after experiment.

2.2.2. Oxidative degradation

A 30 wt % MEA solution, previously loaded with CO_2 (α = 0.4 mole CO_2 / mole MEA), was introduced in an open-batch reactor. Then, the amine solution was heated to 55 °C and sparged with a gas blend of air and 2% CO_2 (0.35 L/min air + 7.5 mL/min CO_2) for 213 h (9 days). The temperature was chosen to be as representative as possible of the classic conditions in the absorber (typically 40 °C for MEA). Samples were taken from the liquid phase and analyzed at regular intervals.

2.3. Analyses

2.3.1. Liquid Chromatography – Mass Spectrometry (LC-MS)

Analyses of the degraded samples were carried out on a LC-MS/MS system, 6460 Triple Quadrupole Mass Spectrometer coupled with 1290 Infinity LC Chromatograph and Infinity Autosampler 1200 Series G4226A from the supplier Agilent Technologies. The molecules were ionized by an electrospray ionization source (ESI). For the quantification of the remaining amine, the samples were diluted to 1/10000 in water and an internal standard, MEA-d*4* ($HO\text{-}CD_2\text{-}CD_2\text{-}NH_2$) was added before injection. A specific method (Selected Ion Monitoring) permitted a higher sensitivity and accuracy.

2.3.2. Gas Chromatography – Mass Spectrometry (GC-MS)

GC-MS analyses were carried out on a Gas Chromatograph 7890A equipped with an Autosampler 7693 and coupled with a mass spectrometer (inert XL EI/CI MSD with triple axis detector 5975C). The Mass Spectrometer allows having both Scan and SIM Mode and could be used in Electronic Impact (EI), Positive and Negative Chemical Ionization (PCI and NCI). Helium was used as carrier gas and methane as reagent gas for chemical ionization (CI). The samples were first diluted in water 1/10 to 1/100 depending on the type of analyses and the level of degradation. They were injected in Split mode to avoid contamination of the system and to have a higher sensitivity. Separation of the different analytes was performed on a CP-SIL-8 CB Amines column (Varian). The main degradation compounds were quantified in EI mode according to calibration curves obtained from commercial standards at different concentrations. When the degradation compound was not commercially available, quantification was estimated and based on a standard with a similar chemical structure.

3. Results and discussion

3.1. Thermal degradation

At 135 °C in the presence of CO_2, MEA degraded 57.6 % after 5 weeks; the slope of the degradation rate was quite linear during the first four weeks, and then started to slow down. In Figure 1 the amine loss is plotted together with the formation of different degradation products. The plot shows to what extent the lost amine is accounted for by the different degradation products (the percentage of formation takes into account the number of nitrogen atoms present into the different degradation products).

The key degradation compounds that have been previously reported [1] were also detected in this study: 2-oxazolidinone **1** (OZD), and *N*-(2-hydroxyethyl)ethylenediamine **2** (HEEDA), *N*-(2-hydroxyethyl)imidazolidinone **3** (HEIA). In addition, one new compound, *N*-(2-aminoethyl)-*N'*-(2-hydroxyethyl)imidazolidinone **4** (AEHEIA), whose structure was suggested by interpreting the mass spectra both in EI and CI mode, was also identified. It can be seen from Figure 1 that the amount of the two imidazolidinones (HEIA and AEHEIA) increases with time, which is an indication of their relative stability. In contrast, the amounts of OZD and HEEDA are constant which suggests that they are intermediate compounds undergoing further reactions. A similar trend was also observed in the recent work done by Davis and Rochelle.[3] The authors also detected *N*,*N'*-bis(2-hydroxyethyl)urea, which is not observed in the present study as a result of our analytical methods not being appropriate for detection of this type of compound.

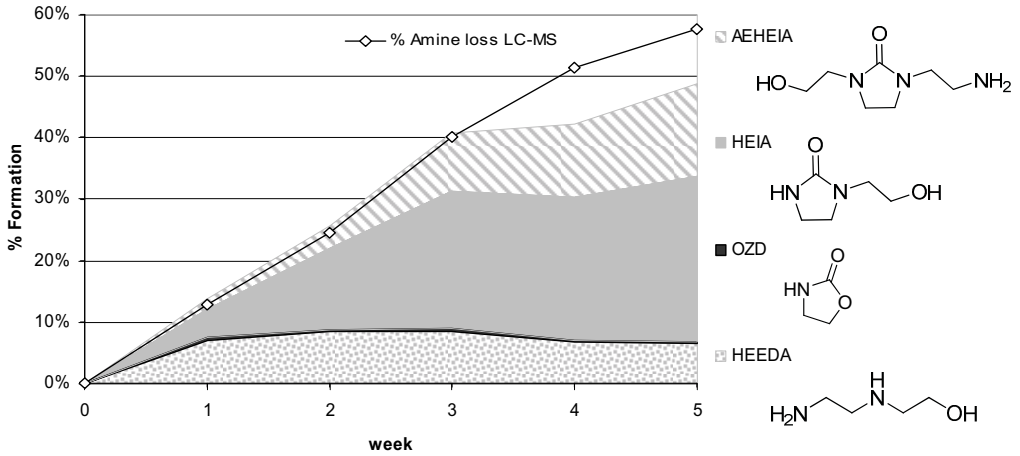

Figure 1. Thermal degradation of MEA (30 wt %, CO_2 loaded, α = 0.5, 135 °C)

The mechanism for thermal degradation of MEA has been the subject of some discussion. It seems accepted that the first step is the oxazolidinone formation by carbamate ring-closure. Then the opinions are divided concerning the order of formation between HEEDA **2** and HEIA **3**. In 1984, Kim and Sartori studied the thermal degradation of DEA and suggested that the dimer would be obtained by opening of the corresponding oxazolidinone with another DEA molecule.[9] By analogy, Davis and Rochelle came to the same conclusions regarding the degradation mechanism of MEA: HEEDA **2** would be obtained by OZD **1** opening and would react again with CO_2 to give HEIA **3**.[3] This last reaction can also be supported by a recent study which showed the complete instability of HEEDA in the presence of CO_2 with HEIA as the major degradation compound.[10] Concerning AEHEIA **4**, its formation could be explained in the same way; HEEDA reacts with the oxazolidinone to give the trimer, which, in the presence of CO_2, can give this imidazolidinone. The general pathway for the thermal degradation of MEA is represented in Figure 2.

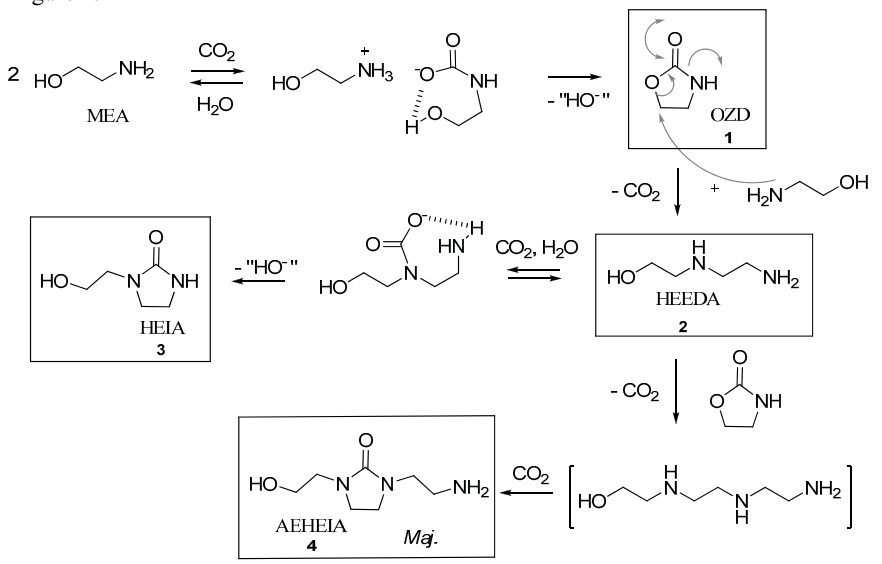

Figure 2. Proposed mechanism for the thermal degradation of MEA

3.2. Oxidative degradation

MEA degraded at 5.8 % after 9 days in the oxidative degradation experiment. As in the previous section, Figure 3 shows the percentage of formation of the main degradation compounds by taking into consideration the number of nitrogen atoms contained into the molecule. In this case, the overall level of degradation was quite low and the calculated degradation rates are less accurate.

The only shared product with the thermal degradation is OZD **1**, whose formation can be accounted for by the same mechanism, i.e. by carbamate ring-closure. However, the two main degradation compounds are *N*-(2-hydroxyethyl)formamide **6** (HEF) and *N*-(2-hydroxyethyl)imidazole **5** (HEI).[11] The former can be explained by reaction of MEA with formic acid, while the mechanism of formation of HEI is still unknown.

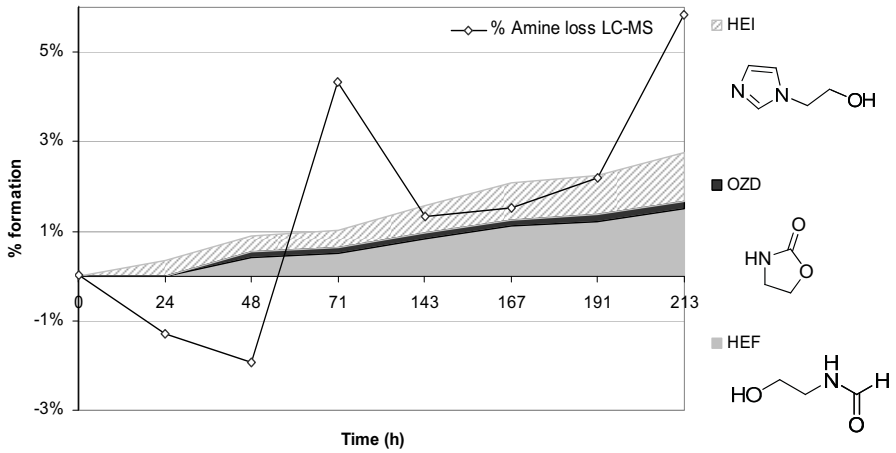

Figure 3. Oxidative degradation of MEA (30 wt %, CO_2 loaded, α = 0.4, sparged with air (0.35 L/min) + 2% CO_2 (7.5 mL/min))

3.3. MEA degradation in pilot plant

3.3.1. Results

The laboratory MEA thermal and oxidative degradation results were compared with results from the MEA campaign performed in the pilot plant at Esbjerg. In Figure 4, the GC-MS chromatograms obtained for the thermal and oxidative degradation of MEA are compared with the final lean MEA solution from Esbjerg. More degradation products are observed in the sample from Esbjerg than in the lab-scale experiments.

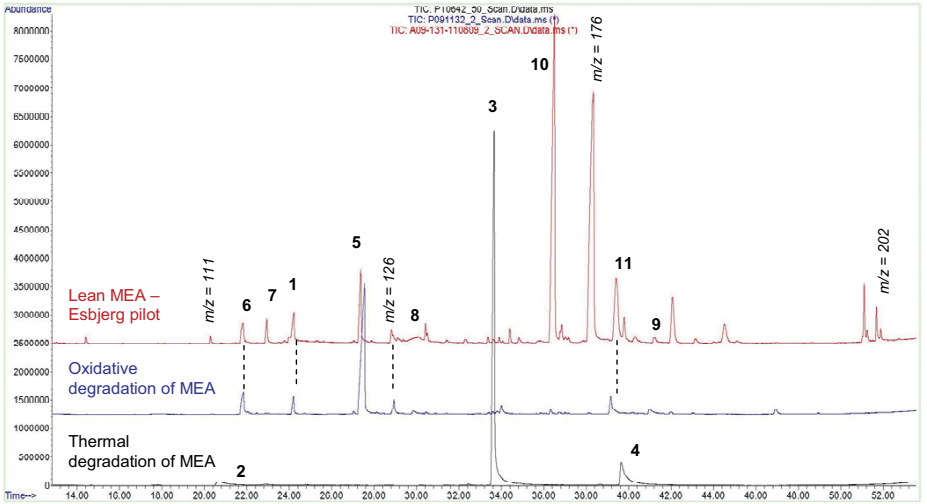

Figure 4. GC-MS chromatograms of the degraded MEA solutions in the two lab-experiments in comparison with the lean MEA solution from the Esbjerg plant

It can be seen from Figure 4 that the contribution of thermal degradation in the real samples appears to be quite limited: HEIA **3** was identified but in a very small amount and, surprisingly, HEEDA **2** was not detected in the pilot sample. This point is in agreement with Strazisar's observation in the analysis of degraded MEA in another capture plant.[7]

On the other hand, the same products as those obtained during the oxidative degradation experiment were found: OZD **1** and HEI **5** were positively identified as well as HEF **6.** However, the identification of these three products does not account for all MEA degradation under real CO_2 capture conditions since a greater number of peaks were observed. In fact, other amide derivatives were identified. *N*-(2-hydroxyethyl)acetamide **7** (HEA) was discovered in a not negligeable amount while 2-hydroxy-*N*-(2-hydroxyethyl)acetamide **8** (HHEA) and *N*,*N'*-bis(2-hydroxyethyl)oxalamide **9** (BHEOX) were traced.

In addition, two major products were identified being 4-(2-hydroxyethyl)piperazin-2-one **10** (HEPO) and *N*-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide **11** (HEHEAA). (See Appendix A) The structure of the first one was confirmed by comparison with the standard. For the second one, an experiment performed in the lab by mixing (2-hydroxyethyl)glycine with MEA permitted suggesting this structure. The empirical formula was also confirmed by Q-TOF analysis ($C_6H_{14}N_2O_3$). These two last products were also identified as main degradation compounds in the work by Strazisar et al.[7]

3.3.2. Mechanistic studies

Since MEA has been found to react with HCOOH to give HEF, we also suspect that there could be similar reactions between MEA and other carboxylic acids. While we have not analyzed for carboxylic acids in the present work, it is known from the literature that formic, acetic, glycolic and oxalic acids are formed during oxidative degradation of MEA.[4,12] We believe products **7**, **8** and **9** (shown in Figure 5) are formed by reaction of MEA with respectively acetic, glycolic and oxalic acids. This result is supported by a synthesis study done by Zamudio-Rivera et al.[13] 2-hydroxy-*N*-(2'-hydroxyalkyl)acetamide derivatives were quantitatively synthesized in experimental conditions close to what are encountered in the absorber (80°C for 3h with a 80-95% yield). We used this protocol to synthesize at lab-scale HEA **7** and HHEA **8** by mixing MEA with respectively acetic and glycolic acids. The reaction products were not purified but compared with the pilot samples. Concerning the reaction of oxalic acid with MEA, the intermediate compound is not detectable in GC-MS; however, the product concerning the double formylation BHEOX **9** was identified in the pilot samples by matching with the commercial standard. The present

results strongly suggest that carboxylic acids not only are formed during MEA degradation, but also play a role in further degradation of the solvent.

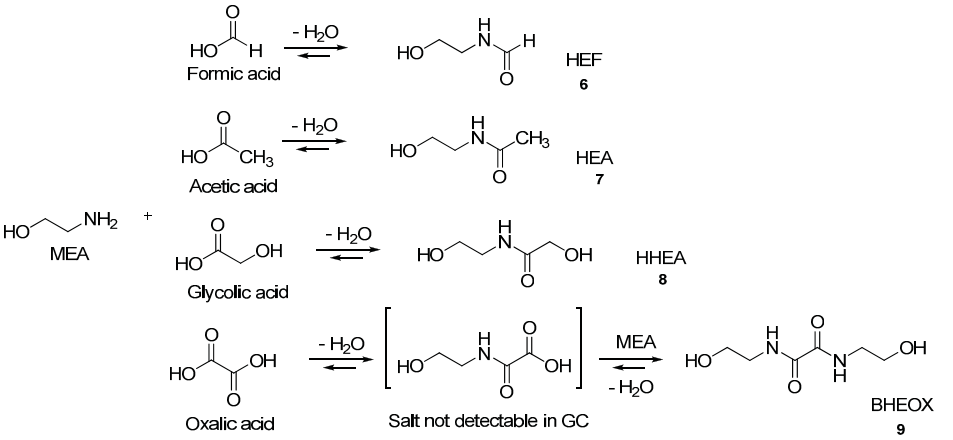

Figure 5. Reaction of MEA with the different carboxylic acids

Concerning the formation of HEPO **10**, Strazisar et al. suggested a mechanism based on the dehydration of HEHEAA **11**.[7] The amine function is more nucleophilic than the amide function, which explains why the product 4-(2-hydroxyethyl)piperazin-2-one is expected to be the major product with regard to its isomer 1-(2-hydroxyethyl)piperazin-2-one.

4. Conclusion

Comparison of lab-scale experiments with degradation in the Esbjerg pilot plant suggests that oxidative degradation is the dominant form of degradation in the plant. All the compounds detected for the oxidative degradation (HEF, OZD and HEI) were also found in the pilot solvent while few compounds relating to the thermal degradation of MEA (HEIA) were detected.

The present results also suggest that carboxylic acids play a significant role in degradation in CO_2 capture plants. They react with MEA to give amide derivatives (HEF, HEA, HHEA, BHEOX). Other complex products are also obtained (HEPO, HEHEAA) by successive reactions probably from these amides derivatives. Work is still ongoing to conclusively identify all the main degradation products and to understand all main reaction mechanisms. In the future we also intend to investigate the reactivity of MEA with aldehydes.

Acknowlegments

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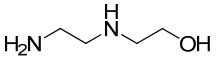
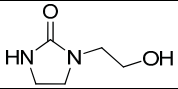
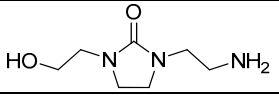
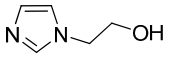
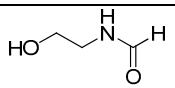
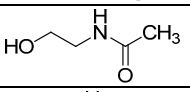
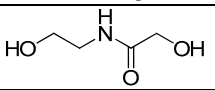
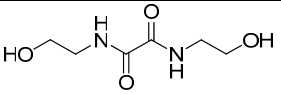
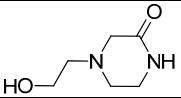
Appendix A. Summary of the degradation compounds

N°	Abb.	Name	CAS Number	Structure
1	OZD	2-oxazolidinone	497-25-6	
2	HEEDA	*N*-(2-hydroxyethyl)ethylenediamine	111-41-1	
3	HEIA	*N*-(2-hydroxyethyl)imidazolidinone	3699-54-5	
4	AEHEIA	*N*-(2-aminoethyl)-*N'*-(2-hydroxy-ethyl)imidazolidinone	/	
5	HEI	*N*-(2-hydroxyethyl)imidazole	1615-14-1	
6	HEF	*N*-(2-hydroxyethyl)formamide	693-06-1	
7	HEA	*N*-(2-hydroxyethyl)acetamide	142-26-7	
8	HHEA	2-hydroxy-*N*-(2-hydroxyethyl)acetamide	3586-25-2	
9	BHEOX	*N*,*N'*-bis(2-hydroxyethyl)oxalamide	1871-89-2	
10	HEPO	4-(2-hydroxyethyl)piperazin-2-one	23936-04-1	
11	HEHEAA	*N*-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide	144236-39-5